

IN THE U.S. PATENT AND TRADEMARK OFFICE

APPLICANT: Kazuaki SAKAKI et al.

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FOR: RARE-EARTH SINTERED MAGNET AND  
METHOD OF MANUFACTURE

ART UNIT: 1793

EXAMINER: SHEEHAN, JOHN P

D E C L A R A T I O N

Honorable Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir,

I, Kazuaki SAKAKI, resident of c/o Magnetic  
Materials Research Center, Shin-Etsu Chemical Co.,  
Ltd., 1-5, Kitago 2-chome, Echizen-shi, Fukui-ken,  
Japan do hereby declare that:

1. I was graduated from Department of  
Chemistry, Faculty of Science, Kanazawa University,

Japan in March 1991. Since April 1991, I have been employed by Shin-Etsu Chemical Co., Ltd., the assignee of the above-identified application. I have been engaged in research and development relating to rare earth magnet materials in the laboratory of the Company.

2. I am one of the named inventors of the above-identified application and hence, am familiar with the subject matter disclosed in said application.

3. In order to show the feature of the present invention, I conducted the following experiments.

**[Experiment]**

**Comparison No. 1**

Sintered magnets were produced in the same composition and by the same method as in Example 5 in the specification of the above-identified application. As in Example 5, magnets measuring  $5 \times 5 \times 5$  mm were cut from the resulting sintered magnets.

Next, a 10  $\mu\text{m}$  layer of nickel and a further 10  $\mu\text{m}$  layer nickel were electroplated in this order onto the resulting sintered magnets.

Nickel electroplating was carried out using a plating bath adjusted to concentrations of 40 g/L nickel chloride, 270 g/L nickel sulfate and 30 g/L boric acid, and at a bath temperature of 50° C and a current density of 2.0 A/dm<sup>2</sup>. This was followed by another nickel electroplating step under the same conditions as the first nickel plating step. The plated magnets were subsequently heat treated at 300° C for 50 hours in air (oxygen partial pressure, 20 kPa), slowly cooled to room temperature, yielding hydrogen gas test specimens. The magnetic properties of the resulting hydrogen gas test specimens were measured with a VSM.

The hydrogen gas test specimens were each placed in a pressure vessel and subjected to a hydrogen gas test under the following conditions: hydrogen, 5 MPa, 25° C, one day. Following the test, the magnets were removed, their appearance was visually checked, and their magnetic properties were measured with a VSM.

### Comparison No. 2

Sintered magnets were produced in the same composition and by the same method as in Example 5 in the specification of the above-identified application. As in Example 5, magnets measuring 5 × 5 × 5 mm were cut from the resulting sintered magnets.

Next, a 10  $\mu\text{m}$  layer of nickel and a further 10  $\mu\text{m}$  layer nickel were electroplated in this order onto the resulting sintered magnets as in Comparison No. 1.

The plated magnets were subsequently heat treated at 300°C for 50 hours in air (oxygen partial pressure, 20 kPa), slowly cooled to room temperature, then coated by spraying on an epoxy resin at a thickness of 20  $\mu\text{m}$ , yielding hydrogen gas test specimens. The magnetic properties of the resulting hydrogen gas test specimens were measured with a VSM.

The hydrogen gas test specimens were each placed in a pressure vessel and subjected to a hydrogen gas test under the following conditions: hydrogen, 5 MPa, 25°C, one day. Following the test,

the magnets were removed, their appearance was visually checked, and their magnetic properties were measured with a VSM.

The results are shown in Tables I and II. The results of Examples 5 and 6 and Comparative Examples 7 to 10 in the specification of the above-identified application are also shown in Tables I and II.

**Table I**

		Surface treatment conditions	Hydrogen gas test conditions	Appearance after hydrogen gas test	Thickness of surface layer
Example	5	Cu(5 $\mu\text{m}$ )-Ni(5 $\mu\text{m}$ )-Ni(10 $\mu\text{m}$ ) plating + 300°C, 50-hour heat treatment (O <sub>2</sub> : 20 kPa) + epoxy resin coating	10 MPa 25°C 1 day	no change	2 $\mu\text{m}$
	6	Cu(5 $\mu\text{m}$ )-Ni(5 $\mu\text{m}$ )-Ni(10 $\mu\text{m}$ ) plating + 250°C, 3-hour heat treatment (O <sub>2</sub> : 1 $\times$ 10 <sup>-2</sup> Pa) + epoxy resin coating		no change	0.5 $\mu\text{m}$
Comparative Example	7	not surface treated (only epoxy resin coating)		disintegrated	-
	8	Cu(5 $\mu\text{m}$ )-Ni(5 $\mu\text{m}$ )-Ni(10 $\mu\text{m}$ ) plating + epoxy resin coating		disintegrated	-
	9	Cu(5 $\mu\text{m}$ )-Ni(5 $\mu\text{m}$ )-Ni(10 $\mu\text{m}$ ) plating + 50°C, 12-hour heat treatment (O <sub>2</sub> : 20 kPa) + epoxy resin coating		disintegrated	not measurable*
	10	Cu(5 $\mu\text{m}$ )-Ni(5 $\mu\text{m}$ )-Ni(10 $\mu\text{m}$ ) plating + 800°C, 12-hour heat treatment (O <sub>2</sub> : 20 kPa) + epoxy resin coating		no change	18 $\mu\text{m}$
	1	Ni(10 $\mu\text{m}$ )-Ni(10 $\mu\text{m}$ ) plating + 300°C, 50-hour heat treatment (O <sub>2</sub> : 20 kPa)	5 MPa 25°C 1 day	disintegrated	2 $\mu\text{m}$
	2	Ni(10 $\mu\text{m}$ )-Ni(10 $\mu\text{m}$ ) plating + 300°C, 50-hour heat treatment (O <sub>2</sub> : 20 kPa) + epoxy resin coating		disintegrated	2 $\mu\text{m}$

\*An oxide layer did form, but it was too thin to be measured.

Table I shows the heat treatment conditions, the hydrogen gas test conditions, and the appearance of the magnets following the hydrogen gas test. In Examples 5 and 6 and Comparative Example 10, no change occurred in the hydrogen gas test. However, in Comparative Examples 7, 8 and 9, and Comparisons Nos. 1 and 2, the magnet disintegrated into small pieces. It is noted that the magnets of Comparisons Nos. 1 and 2 would more easily disintegrate when the hydrogen gas test is conducted in 10 MPa since they were disintegrated even on the test in 5 MPa.

Table II shows the magnetic properties of the magnets before surface treatment and before and after the hydrogen gas test.

Table II

		Before surface treatment			Before hydrogen gas test			After hydrogen gas test		
		Br (kG)	iHc (kOe)	(BH) <sub>max</sub> (MGoe)	Br (kG)	iHc (kOe)	(BH) <sub>max</sub> (MGoe)	Br (kG)	iHc (kOe)	(BH) <sub>max</sub> (MGoe)
Example	5	11.85	17.05	34.0	11.74	16.88	32.7	11.75	16.85	32.7
	6	11.83	17.21	33.9	11.72	16.99	32.6	11.71	17.02	32.6
Comparative Example	7	11.92	16.77	34.4	11.80	16.52	33.0			
	8	11.88	16.85	34.2	11.77	16.63	32.9			
	9	11.85	17.01	34.0	11.72	16.95	32.6			
	10	11.84	17.12	34.0	11.75	10.15	17.2	11.72	10.23	17.2
Comparison No.	1	11.86	17.19	34.1	11.68	13.33	28.6			
	2	11.85	17.22	34.1	11.65	13.40	28.5			

Table II shows the magnetic properties of the magnets before surface treatment and before and after the hydrogen gas test. In Examples 5 and 6 according to the invention, the magnetic properties of the magnets remained substantially unchanged before surface treatment and before and after the hydrogen gas test. In Comparative Examples 7 to 10 and Comparisons Nos. 1 and 2, the magnets disintegrated as a result of hydrogen treatment, making it impossible to measure the magnetic properties following hydrogen treatment.

### Comparison No. 3

Sintered magnets were produced in the same composition and by the same method as in Example 7 in the specification of the above-identified application. As in Example 7, magnets measuring 5 × 5 × 5 mm were cut from the resulting sintered magnets. A 20  $\mu\text{m}$  layer of nickel were electroplated onto the resulting magnets under the same conditions as in Example 7. That is, nickel electroplating was carried out using a plating bath adjusted to concentrations of 40 g/L nickel chloride, 270 g/L nickel sulfate and 30 g/L boric acid, and at a bath temperature of 50°C and a current density of 2.0 A/dm<sup>2</sup>. The plated magnets were subsequently heat treated at 350°C for 50 hours in air, then slowly cooled to room temperature, yielding hydrogen gas test specimens. The magnetic properties of the test specimens were measured with a VSM.

The hydrogen gas test specimens were each placed in a pressure vessel and subjected to a hydrogen gas test under the following conditions: hydrogen, 5 MPa, 25°C, three days. Following the

test, the magnets were removed, their appearance was visually checked, and their magnetic properties were measured with a VSM.

#### Comparison No. 4

Sintered magnets were produced in the same composition and by the same method as in Example 7 in the specification of the above-identified application. As in Example 7, magnets measuring 5 x 5 x 5 mm were cut from the resulting sintered magnets. A 20  $\mu\text{m}$  layer of nickel were electroplated onto the resulting magnets under the same conditions as in Comparison No. 3. The plated magnets were subsequently heat treated at 350° C for 50 hours in air, slowly cooled to room temperature, then coated by spraying on an epoxy resin at a thickness of 20  $\mu\text{m}$ , yielding hydrogen gas test specimens. The magnetic properties of the test specimens were measured with a VSM.

The hydrogen gas test specimens were each placed in a pressure vessel and subjected to a hydrogen gas test under the following conditions: hydrogen, 5 MPa, 25° C, three days. Following the

test, the magnets were removed, their appearance was visually checked, and their magnetic properties were measured with a VSM.

The results are shown in Tables III and IV. The results of Examples 7 and 8 and Comparative Examples 11 and 12 in the specification of the above-identified application are also shown in Tables III and IV.

Table III

Comparison No.	Example	Surface treatment conditions	Hydrogen gas test conditions	Appearance after hydrogen gas test	Thickness of surface layer
Comparative Example	7	Cu(10 $\mu\text{m}$ )-Ni(10 $\mu\text{m}$ ) plating + 350°C, 50-hour heat treatment in air	5 MPa 25°C 3 days	no change	4 $\mu\text{m}$
	8	Cu(10 $\mu\text{m}$ )-Ni(10 $\mu\text{m}$ ) plating + 300°C, 2-hour heat treatment in air		no change	0.5 $\mu\text{m}$
	11	not surface treated		disintegrated	-
	12	Cu(10 $\mu\text{m}$ )-Ni(10 $\mu\text{m}$ ) plating		disintegrated	-
	3	Ni(20 $\mu\text{m}$ ) plating + 350°C, 50-hour heat treatment in air		disintegrated	4 $\mu\text{m}$
	4	Ni(20 $\mu\text{m}$ ) plating + 350°C, 50-hour heat treatment in air + epoxy resin coating		disintegrated	4 $\mu\text{m}$

Table IV shows the magnetic properties of the magnets before surface treatment and before and after the hydrogen gas test.

Table IV

		Before surface treatment			Before hydrogen gas test			After hydrogen gas test (5 MPa, 25°C, 3 days)		
		Br (kG)	iHc (kOe)	(BH) <sub>max</sub> (MGOe)	Br (kG)	iHc (kOe)	(BH) <sub>max</sub> (MGOe)	Br (kG)	iHc (kOe)	(BH) <sub>max</sub> (MGOe)
Example	7	13.05	14.98	41.2	13.01	14.35	40.6	13.02	14.38	40.6
	8	13.11	14.65	41.6	13.03	14.55	40.7	13.01	14.52	40.7
Comparative Example	11	13.08	14.77	41.4	13.06	14.75	41.2			
	12	13.05	14.50	41.2	13.00	14.33	40.7			
Comparison No.	3	13.10	14.72	41.4	12.95	10.32	35.3			
	4	13.08	14.66	41.3	12.96	10.40	35.5			

In Examples 7 and 8 according to the invention, the magnetic properties of the magnets remained substantially unchanged before surface treatment and before and after the hydrogen gas test. In Comparative Examples 11 and 12 and Comparisons Nos. 3 and 4, the magnets disintegrated as a result of hydrogen treatment, making it impossible to measure the magnetic properties following hydrogen treatment.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated this 17<sup>th</sup> day of April , 2008

Kazuaki Sakaki